TECHNICAL REPORT
66-56-CD

MIGRATION OF FLEXIBLE PACKAGING COMPONENTS INTO FOODS.

by

Robert L Ferm

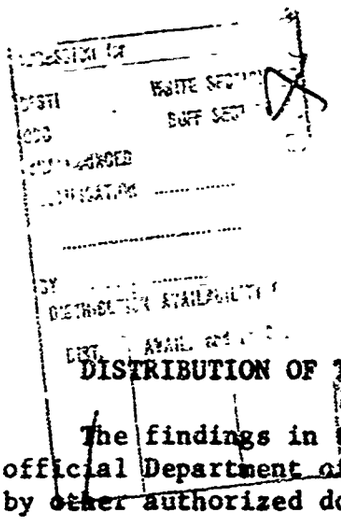
The Pillsbury Company
Minneapolis, Minnesota

Contract No. DA-19-129-AMC-384 (N)

June 1966

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Container Division



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FOREWORD

This contract was originally funded under Task 02, Project 1M643324D587, 64133241 and transferred 1 July 1965 to 1M624101D552, 62141011.

The work was carried out under a work unit to design a family of lightweight, nonrigid packages for processed foods. Knowledge was sought to establish procedures and develop data to assure that selected packaging materials can be safely used from an extractive standpoint at high processing temperatures, 250°F. and above. Heat-processed foods in flexible packages are being introduced in the military feeding system in the Operational Rations, namely, in the "M" Packet and Meal, Ready-to-Eat, Individual.

The investigation described herein was performed in the Research and Development Laboratories of The Pillsbury Company, 311 Second Street, S.E., Minneapolis 14, Minnesota. Mr. Robert L. Ferm served as the Official Investigator. His collaborators were Endel Jaska, John Slavics, Helen Fett, Kenneth Parlour, Telford Norvold and William Bosin.

Project Officer for the U. S. Army Natick Laboratories was Mr. Joseph Szczeblowski of the Packaging Research Branch, Container Division. The Alternate Project Officer was Mr. Gerald L. Schulz, Packaging Research Branch, Container Division.

EDWARD A. NEBESKY
Chief
Container Division

APPROVED:

DALE H. SIELING, Ph.D.
Scientific Director

W. M. MANTZ
Colonel, QMC
Commanding

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SUMMARY

Four different foil-laminated, flexible film materials, potentially suitable for packaging and heat processing of foods, were investigated with respect to the migration of film residues into the food during heat processing. Specific objectives of the investigation were:

(1) To determine the amounts of film extractives which migrate into food simulating solvents,

(2) To determine the nature and source of any extractives found,

(3) To determine the amounts of volatile extractives which may be lost in the determination of solvent extractives,

(4) To develop methods for determining film extractives in fats or oils after high temperature extractions of the films by fat and,

(5) To establish a correlation between the amounts of solvent extractives obtained at 150°F. to the amounts of fat extractives obtained at the highest temperatures compatible with the films.

Extraction methods used and results obtained are presented for n-heptane and water film extractions made at several extraction conditions. The effects of extraction time and temperatures and extraction procedure variations are presented. Similarly, methods and results in determining volatile extractives are given. Results are also presented on evaluations of microscopic alterations in film structure following solvent extractions.

Several procedures for determining film extractives in fat were evaluated and general results of these trials are presented. Specific results on determinations of film extractives in high temperature fat extracts are given and the corresponding comparisons of solvent and fat extraction results are shown.

I. INTRODUCTION:

Flexible packaging containers, when exposed to conditions of food processing and/or sterilization of foods therein, are subject to migration or leaching of packaging components into the food. This project is concerned with this potential migration. More specifically, this study is concerned with evaluating portions of existing test procedures used for determining this migration of packaging substances. Particular reference is made to migrations at high temperature processing conditions and notably with foods or simulated foods having high fat contents.

Federal Regulation safety requirements for polymeric food containers such as flexible packaging films, are specified in Section 121.2514 of the Federal Food, Drug and Cosmetic Act. The test methods outlined in this section are, in part, the subject of this study. Particular emphasis is given to development of methods to correlate the amount of film extractives obtained with simulated foods (solvents) and the amounts obtained with fats or fat and water emulsions. Specific objectives of the project include:

(a) Determine the total amount of extractable materials from specific packaging films by selected solvents at selected conditions of extraction.

(b) Determine the nature and source of any extractables found in objective (a).

(c) To evaluate the possible losses of volatile extracted film materials during the determination of solvent extractives. If losses are evident, develop procedures to quantitate such losses.

(d) To develop methods for determining extractives from films by fat when the fat has been in contact with the packaging films at conditions of high temperature processing. (The same films as in objective (a) to be used.)

(e) To establish the ratio between the extractability of solvents at given conditions of extraction to the extractability of fats at conditions more rigorous than for solvents. (Fat extractions to be the highest temperature compatible with the film under test.)

II. EXTRACTIONS BY FOOD SIMULATING SOLVENTS:

A. Introduction

All film materials included in this study were extracted according to Section 121.2514 of the Federal Food, Drug and Cosmetic Act, Test Conditions A (1). Normal

heptane and water are the solvents specified in these extraction tests and the procedures used for carrying out the mechanics of extraction are essentially the same for both solvents. In addition to the stated Section 121.2514 methods, all films were extracted with modified temperature conditions to increase extraction yields. Extractions so made were sought for further qualitative studies of the residues. Extractions with other variations in Section 121.2514 parameters were also made to study effects of extraction variables and equipment or apparatus used.

Only supported films (films applied to aluminum foil) are included in this study and therefore, a single extraction method for this one type of sample was desired. Initial consideration was given to only two extraction procedures -- extraction cells and pouch extractions (extracting solvent sealed within a film pouch). Of these, only pouch extractions were used for a number of reasons: Karel and Wo[illegible]n (2) reported solvent losses using extraction cells with laminated films. Leaking pouches are more readily discerned and evaluated than cells. Also, the possible contamination from cell spacers and/or gaskets, particularly at high temperature extractions, are eliminated with pouches. Additionally, many more extractions in a given time period are possible with pouches. Cell extractions are equipment limited. Finally, the pouch system is a more realistic approach since the ultimate food packaging use for these films would be in pouch form.

The extraction procedure used throughout this study involves heating selected solvents sealed within a pouch of the film under test at specific temperatures for a specific period of time. The solvent is then cooled, removed from the pouch and evaporated off. Extracted residues remaining are determined gravimetrically.

The chloroform soluble residue tests of Section 121.2514 methods were not performed with any film residues obtained in this study since all films gave total residues considerably lower than acceptable limits established by the Food and Drug Administration.

B. Equipment and Procedures

1. Packaging Films

A number of supported film and film combination samples were obtained for screening and selection of experimental samples. All were obtained directly from the film manufacturers or from intermediate contract laminating firms. Screening was done

to determine the applicability of these films to high temperature processing. In all, ten film materials were screened in two ways:

(a) 1 x 4 inch strips of each film were cut and suspended in a 300°F. vegetable oil bath for periods of from 20 minutes to 2 hours and visually observed at 10 minute intervals.

(b) 1 x 4 inch strips of each film were cut and suspended in a 300°F dry oven for 20 minutes and visually observed.

From screening results obtained and also to obtain additional data on some films not screened, principals of this contract and representatives of the Federal Food and Drug Administration selected four films for initial extractive investigations. These are listed below with the contractors' source of supply.

(a) Lexan Polycarbonate - A co-polymer resin of p,p' isopropylidene diphenol and carbonyl chloride, manufactured by General Electric Co., Pittsfield, Mass., and laminated by Reynolds Aluminum Co., Richmond, Va.

(b) Rilsan-Nylon 11 - A condensation polymer of 11-amino undeconoic acid manufactured by May Industries, Atlanta, Ga., and laminated by Reynolds Aluminum Co., Richmond, Va.

(c) Kodar Polyester - A mixed polymer of 1,4-cyclohexylene dimethylene terephthalate and 1,4-cyclohexylene dimethylene isophthalate manufactured by Eastman Chemical Products, Kingsport, Tenn., and laminated by G.T. Schjeldahl Co., Northfield, Minn.

(d) Aclar-Fluorocarbon (not included in initial screening) - A co-polymer of chlorotrifluoroethylene and vinylidene fluoride manufactured by Allied Chemicals, Morristown, N.J., and laminated by G.T. Schjeldahl Co., Northfield, Minn.

Evaluation of the Aclar-Fluorocarbon film obtained was discontinued early in the study when it failed repeatedly in several initial experiments. It is not known if this is peculiar only to the sample obtained. It was replaced in the experimental trials with another fluorocarbon film identified as follows:

(e) FEP Teflon-Fluorocarbon - A completely fluorinated ethylene-propylene co-polymer manufactured by E.I. du Pont de Nemours, Wilmington, Del., and laminated by

G.T. Schjeldahl Co., Northfield, Minn.

All films studied were 2 mils thick and were applied to 0.35 gauge aluminum foil.

Other films screened but not included in additional studies were:

1. Milprint Combination - Polypropylene inside, mylar outside, foil between.
2. Dow Combination 1302 - Polyvinyl inside, outside unknown, foil between.
3. Schjeldahl Capron Nylon.
4. Dow Combination - Polyethylene inside, mylar outside, foil between.
5. Dow Combination - Polyethylene inside, "aquatuf" outside, foil between.

2. Extraction Solvents

(a) Water

The water used in all extraction procedures was demineralized and double distilled. The demineralizer used was a Barnstead Model FR-2, anion and cation double bed system and the first distillation was through a Barnstead Model ELQ automatic still. The second distillation was through an all glass, laboratory still. All water used had a conductivity of less than 0.4 micromhos.

Blank residue determinations were made on this water and the total residue was found to be 2.0 $\pm$0.1 mg/liter.

(b) n-heptane

All heptane used for extractions was Fisher Certified, Spectro analyzed n-heptane. Residue blank determinations showed residues of 0.6 mg/liter.

3. Procedure for Preparing Pouches

(a) Equipment

1. Robot Model RT-I, air operated jaw sealer manufactured by Pack-Rite Machines, Milwaukee, Wisc. This sealer was used both with 3/4 inch wide flat bar jaws, teflon coated, and curved surface jaws diagrammed in Figure 1. The curved surface jaws were patterned after the study of Christie, Bolze and Medved (3).

2. Thermal Impulse Heat Sealer, Model 14A, manufactured by the Vertrod Corporation, Brooklyn, New York.

3. Scott Tensil Strength Tester, Model J-1, manufactured by Scott Testers Inc., Providence, R.I.

(b) Pouch Preparation

Pouches were formed by overlaying 2 sized, rectangular pieces of film (foil side out) and heat sealing three adjoining sides in the Robot sealer. Following careful measurement of the exposed internal surface, a specific volume of solvent (water or heptane) was placed in the pouch. The fourth side was then sealed after compressing the pouch to exclude the maximum amount of air.

A constant solvent volume to total exposed film surface area of 2 ml/in^2 was maintained in all extractions (water and heptane) except in special trials. Volumes of 0.5, 1.0 and 1.5 ml/in^2 were used in these limited experiments with water only. Solvent weights for each pouch were calculated from the density and volume of the solvent used.

Pouch sizes of 4.5 x 6.5 inches and 3.5 x 5.5 inches were used throughout. The latter sized pouch was used with some extractions of Kodar-Polyester and Teflon-Fluorocarbon films whose heat seals tended to rupture, part or crack during elevated temperature extractions. These smaller pouches were sealed within a Mylar-foil laminated pouch for these high temperature extractions which gave sufficient resistance to internal pouch pressure to prevent seal rupture.

The most satisfactory heat sealing conditions found for the films used in this study are shown below.

Film Material	Sealing Variables for Curved Bar Sealer		
	Jaw Pressure (psig)	Jaw Temperature (°F.)	Dwell Time (seconds)
Aclar-Fluorocarbon*	20	400	2.0
Kodar-Polyester	15	465	0.5
Lexan-Polycarbonate	50	420	3.0
Rilsan-Nylon 11	60	450	0.5
Teflon-Fluorocarbon	15	495	0.5
Mylar-Overwrap Pouch	40	325	1.0

*Heat seals obtained were significantly weaker relative to all other films shown.

4. Extraction Procedures at 150°F. Heptane Solvent Only

(a) Equipment

A simple water filled 20 quart cooking vessel was used as a source of heat. This vessel was placed on a variable temperature electric hot plate which was controlled to ±0.5°F. with a Minneapolis Honeywell Versa-Trans Relay and Thermistor Sensor. Bath agitation was provided by a variable speed laboratory stirrer. A wire rack, completely immersed in the bath, and capable of holding 17 pouches, was used to separate the pouches from each other during extraction.

(b) Method

The bath was filled with tap water at 80°F. The wire rack containing the heptane-filled pouches were immersed and heating begun. When the bath attained 150°F. (in 15 ±2 minutes), timing was begun and the temperature was maintained at 150°F. for 2 hours. The rack of samples was then removed from the bath and the sample pouches were allowed to cool to room temperature.

Each pouch was carefully inspected for leaks and dried thoroughly on the outside with a lint free towel. A corner of each pouch was snipped off with a scissors and the solvent drained through Whatman number 42 filter paper into a clean 400 ml beaker. Filtering was done to remove lint present on all film surfaces when received. Four pouches were composited to make one sample. The replicate samples were covered loosely with clean aluminum foil to exclude dust contamination and evaporated on a steam bath to approximately 100 ml. The extract was then transferred quantitatively to a clean, tared platinum dish, evaporated to 2-3 ml on a low temperature hot plate and finally dried in a 100°C. oven for 30 minutes. The platinum dishes were cooled in a desiccator for 30 minutes before weighing the residues to the nearest 0.1 mg. The total extracted residues were calculated as milligrams per square inch of pouch surface and as ppm of solvent weight used for extraction.

(c) Variations in Method

1. To evaluate the amount of extractives obtained as a function of extraction time and also to provide additional extractive materials for qualitative identification, four films were also extracted as described above except that the total

extraction time was extended from 2 hours to 16 hours.

2. To evaluate the possible losses of extracted residues in glass evaporation containers, solvent was evaporated as described above and also by performing all evaporations from tared platinum dishes. Additionally, comparative evaporations were made where all evaporation steps were done entirely in glass containers Results of these trials are shown in Table V and are discussed in the results section below.

5. Extraction Procedures at 250°F. or Above

According to Test Conditions A, Section 121.2514 of federal regulations, only extractions with water are required at 250°F. In this study, extractions with n-heptane were also made at these elevated temperatures to purposely increase heptane extraction yields. Heat processing during extractions were essentially the same for both solvents. Post-heat processing procedures were slightly different for water, and these are described below. Heptane extracts were treated exactly as previously described for 150°F. extractions.

(a) Equipment

A vertical, water filled, pressure retort was used. This retort is equipped with a steam-water heat exchanger and a high speed circulatory pump as a source of heat and cooling. It also has a compressed air inlet for superimposing an internal air pressure in excess of retort water vapor pressure. The retort is capable of maintaining controlled extraction studies up to temperatures of 400°F. and 150 psig pressure with controllable limits of $\pm$2.5°F. at 250°F. Its size and perforated aluminum pouch holding racks permit simultaneous extractions of 81 pouches per run.

(b) Method

The solvent filled pouches (water or heptane) were placed in the pouch holding racks of the retort which is then filled with water. The domed cover was then clamped down and 10 psig air pressure admitted. Heating was then begun by circulating the retort water through the steam-heated exchanger. When the temperature reached its desired level, steam to the heat exchanger was reduced and regulated to maintain a constant temperature for the time desired. At the end of the heating cycle, steam in the heat exchanger was replaced with cold water to cool the retort. When the

retort water temperature cooled to 80°F., the superimposed air pressure was vented and the system opened. The retort water was then drained and the pouches removed. A typical heating and cooling curve for a 250°F. water extraction is shown in Figure 2.

Following heat processing each pouch was carefully inspected for leaks and dried thoroughly on the outside with a lint free towel. A corner of each pouch was snipped off with scissors and the water drained through Whatman number 1 filter paper into a clean 400 ml beaker. Four pouches were composited to make one sample. Replicate samples were covered loosely with clean aluminum foil and evaporated on a low temperature hot plate to approximately 100 ml. The extract was then transferred quantitatively to a clean, tared platinum dish, evaporated further on a low temperature hot plate to 2-3 ml and finally dried in a 100°C. oven for 30 minutes. The platinum dishes were cooled in a desiccator for 30 minutes before weighing the residues to the nearest 0.1 milligram. The total extracted residues were calculated as milligrams per square inch of pouch surface and as ppm of solvent weight used for extractions.

(c) Variations in 250°F. Method

1. Water Extractions

To evaluate the amount of extractives obtained as a function of temperature and also to provide additional extractive material for qualitative identification, all films were also extracted as described above except that the extraction conditions were 275°F. for 2 hours.

2. Heptane Extractions

Both elevated temperatures and extended extraction times were used for heptane extractions, primarily to increase extraction yields. Increased yields were desired both to confirm identifications of residues obtained at lesser concentrations and to obtain residue samples for use in method development on recovering extractives from fat.

6. Infrared Analyses of Residues

Residues of all films examined, obtained by both heptane and water extractions, were analyzed by infrared spectrophotometry for qualitative identification.

All analyses were made on a Beckman IR-4 spectrophotometer in KBr pellets. Additionally, both transmission and Attenuated Total Reflectance Spectra were obtained on samples of each film that were physically delaminated into foil and adhesive-film moieties. Infrared transmission spectra were also obtained on samples of each film before laminating to foil.

7. Microscopic Examination of Extracted Films

All films included in this study were examined microscopically before and after solvent extractions. A Bausch and Lomb Model LI Polarizing Microscope was used. Foil laminations were removed prior to examination by immersing the laminated films in 10% HCl to dissolve the foil followed by thorough water washing. (NaOH immersion was used for Rilsan films as HCl treatment followed by water washing turned the film opaque.)

All microscopic samples were cut from the center of the pouches equidistant from all heat seals. Delaminated samples of about 1 x 1/2 inches were mounted dry between two glass slides and observed at 100X magnification.

8. Determination of Volatile Losses

In the extraction procedures detailed above, any volatile fractions of extracted residues would probably be evaporated and lost during the solvent evaporation steps. Attempts were made in this study to determine the existance of volatile extractives, particularly those components that would be lost at water evaporation temperatures or less.

A direct, gas chromatographic approach was used exclusively. Extraction solvents, sampled directly from the heat processed pouches immediately after extraction were examined by gas chromatography with emphasis on detecting any components not present in solvent blanks. A hydrogen flame ionization detector was used in the gas chromatograph which was capable of detecting volatile components of 0.5 ppm concentration. Heptane extracts, made both at 150°F. and 250°F., were examined.

(a) Equipment

1. An F&M Model 810, dual column, dual hydrogen flame detector gas chromatograph.

Operating Conditions:

Column Temperature:	80°C.
Helium Flow Rate:	60 ml/min
Hydrogen Flow Rate:	60 ml/min
Air Flow Rate:	375 ml/min
Attenuation & Range:	2 x 10
Port Temperature:	175°C.
Detector Temperature:	175°C.
Sample Size:	3-5 microliters

2. Column

6 x 1/4" OD Stainless steel packed with 15% DC Silicone 550 on 85% chromosorb W, 30/60 mesh, acid washed.

3. Hamilton Syringe -- 10 microliter capacity

(b) Method

Pouches were sampled by direct pouch puncture with the syringe and withdrawing a measured amount of solvent. This was injected directly into the gas chromatograph previously set at the conditions shown.

Reference calibration samples were prepared containing 1, 2 and 5 ppm n-pentane in the n-heptane used for extraction. Detectability of 0.5 ppm n-pentane was easily obtained.

C. Results

1. Film Screening

Data showing the results of initial film screening tests are shown in Tables I and II. Chronologically, all films listed were tested before selection of experimental samples except the Aclar-Fluorocarbon and the Teflon-Fluorocarbon. These were included in the study by the selection team mentioned earlier. Aclar was initially chosen but subsequently replaced with Teflon when Aclar failed the screening tests and repeatedly failed in processing trials detailed below.

2. Heat Sealing and Pouch Preparation

Initial extractions were made at low temperatures and the pouch heat

sealing first used was generally satisfactory for these trials. The Aclar-Fluorocarbon film pouches were an exception. They had very weak seals which frequently ruptured during processing. All initial pouches were made on the Robot Heat Sealer using flat sealing bars. Optimum sealing conditions were based on tensil strength tests previously applied to test seals made at varied sealing conditions. The optimum sealing conditions found in these tests were as follows:

Optimum Flat Bar Sealing Conditions

Film	Jaw Pressure (psig)	Jaw Temperature (°F.)	Dwell Time (seconds)
Kodar	15	475	3.0
Rilsan	50	450	1.5
Lexan	20	420	8.0
Aclar	30	415	2.0

Teflon - not sealed with flat bar sealer

Heat seals made with the flat sealing bars at these conditions were very unsatisfactory, however, if used on pouches in high temperature extractions (250°F. or above). At high temperature, the seals showed complete ruptures, cracks, pinhole leaks or combinations of these depending on the film in question. Repeated trials at these and other sealing conditions were generally unsuccessful. Repeated trials were also made using the impulse sealer cited, especially on the fluoro carbon films, but these were also unsuccessful in producing seals that would withstand high temperature extractions.

At the suggestion of the project officer, curved surface heating bars for the bar sealer were made and evaluated. New sealing conditions were required for these bars on all films and optimum conditions found are given in the Procedures Section. It was found that room temperature tensil strength tests of heat seals had little correlation with performance properties of the pouches during high temperature extractions and that empirically established sealing conditions, evaluated by extraction trials, were of more value.

In general, pouch sealing with curved sealing bars was considerably more reliable than with flat bars. The reliability was quite erratic with Kodar-Polyester

and Teflon-Fluorocarbon films in replicate extractions however, and especially in water extractions made above 250°F. These films frequently and unpredictably ruptured at the heat seals. After repeated extraction attempts ended in failure, including trials where solvent volumes to film surface ratios were varied, the problem was overcome by sealing these pouches within Mylar pouches that have reliable, high temperature resistant sealing properties. Without exception, this procedure was successful for all high temperature extractions of these difficult to seal films.

In the solvent extraction portion of this study, the biggest single enigma or problem was obtaining leak-free heat seals especially during high temperature extractions. All films included in the study are amenable to further heat sealing investigation.

3. Results of 150°F Heptane Extractions

(a) Quantitative Results

The complete results of extraction with n-heptane at 150°F. for 2 hours are presented in Table III. These results show that all film materials tested gave residue levels considerably below the maximum acceptable under federal regulations.

Four of the five films tested were extracted with n-heptane at 150°F. for 16 hours. Results of these extractions are shown in Table IV. With the exception of the Lexan-Polycarbonate, amounts extracted in 16 hour extractions are lower than for 2 hour extractions (Table III). The significance of this finding is not known. The extractive levels in either case are quite low, and it is generally concluded from the data that the amount of extractives obtained at 150°F. is not a significant function of time after 2 hours extraction.

(b) Qualitative Results

The residues of 150°F. heptane extractions were examined by infrared spectrophotometry to obtain information on their chemical nature. Results obtained are given below. No differences were observed in residues from either 2 hour or 16 hour extractions.

Film	Infrared Identification
Kodar-Polyester	Very weak spectra obtained, ester groups indicated
Lexan-Polycarbonate	Polymeric, aromatic ester with both ortho and para disubstitution
Rilsan-Polyamide	Polymeric aryl ester with both ortho and para disubstitution
Teflon-Fluorocarbon	Insufficient residue for infrared identification

From the generally known chemical composition of the film materials and the film manufacturer's statements regarding the lack of film additives in the film samples, the extracted residues identified were suspected as foil laminating adhesives. Confirmation of this suspicion was obtained in additional infrared studies described under high temperature extraction results.

(c) Evaluation of Recovery

A residue recovery study was made on 2 film extractives to evaluate possible losses of residue in glass evaporation dishes versus platinum dishes. Extract solvents from 2 Kodar samples and 2 Lexan samples (One sample is the combination of 4 pouches of each film.) extracted at 150°F., were evaporated entirely in platinum dishes and results compared with the normal procedure where glass containers are used first with subsequent transfer to platinum dishes. Results obtained are given in Table V. In another trial on Kodar extractives only, all evaporation was done in glass dishes. Here, final evaporation and drying was done in a 15 ml glass beaker. The result is also given in Table V.

It is evident from the results presented that the drying container is not a limiting factor in residue recovery in the film extractives tested.

4. Results of Extractions Made at 250°F. and Higher

A general observation of all extractions at 250°F. and higher is the change in pouch appearance. The foil applied to the films became discolored and oxidized appearing and was very brittle and flaking to the touch. Frequent delamination was evident. Without exception, all films also became discolored during these high temperature extractions becoming generally light tan to yellow in shade.

(a) Water Extractions

Results of water extractions performed at 250°F. for 2 hours are shown in Table VI. It is evident in the data shown that extractives for all film materials used are significantly lower than the maximum acceptable under federal regulations. Calculated residues contributed by the extraction water only greatly predominate in the Kodar and Lexan extractives, and this is confirmed by infrared examination of the residues described below.

Results of water extractions of all films at 275°F. for 2 hours are shown in Table VII. Comparing these results with results obtained at 250°F. (Table VI) shows a residue increase for all films with increased extraction temperature. The percent increase varies with the different films but residue levels, including the water blank residues, are considerably lower than maximum levels allowed.

(b) Heptane Extractions

Two hundred fifty degree F. extractions for 2 hours with n-heptane were made on all films included in the study. Results are shown in Table VIII. At this temperature, extractives are shown considerably increased over standard extraction temperature results (Table III). However, even at these greatly accelerated extraction temperatures, total residues obtained from 3 of the 4 films are less than tolerable limits using either solvent corrected or uncorrected values. Only the uncorrected Lexan film extract exceeds the 50 ppm residue concentration set by federal regulations and, as presently amended, this uncorrected residue value is not used.

Successful 8 hour extractions with n-heptane were made on Kodar-Polyester and Rilsan-Nylon films. Results of these extractions are also shown in Table VIII. The data indicates that at these extraction conditions, total residue levels are, in part, a function of extraction time. The difference between the 2 hour and 8 hour heptane extractives at 250°F. is purely quantitative however, for the infrared examination of each, presented below, indicates no qualitative differences.

(c) Infrared Examination of Residues

1. Water Extractives

The infrared spectra of 250°F., water extracted residues from

Kodar, Lexan and Teflon films were essentially the same as for water blanks. These residues are inorganic sulfate salts of calcium and magnesium. The Teflon residues show a trace of organic materials but their concentration was too small for identification. The Rilsan film extractives also contain these water blank residues but have identifiable amounts of organic materials. These were again identified as mixed ortho and para disubstituted aryl esters.

Infrared spectra results on 275°F. water extractions of all films were quite similar to 250°F. extraction results. All show predominantly water blank residues, but, in addition, the 275°F. residues of all films show traces of organic material. Except for the Rilsan extractives, identification was not possible beyond the partial assignments as aryl esters. The Rilsan residue spectra confirms the 250°F. extraction residue identification.

2. Heptane Extractives

Yields from 250°F. heptane extractions were considerably larger than at lower extraction temperatures, and the infrared spectra of all film residues were easier to interpret. Also, legitimate comparisons were possible between these high temperature residue spectra and spectra on laminated films and physically delaminated films both by transmission and ATR methods. Results from these comparisons generally confirmed earlier conclusions that heptane extractives from all four films examined in this study are principally from the laminating adhesives. Only the Lexan-Polycarbonate film residues show definite film-related extractives from these high temperature extractions. The Kodar-Polyester film residue source may be partially or entirely film-related since the Kodar film polymer and its laminating adhesive materials are chemically similar.

Infrared identifications of high temperature, heptane extracted residues are given below:

Film	Infrared Identification of Extracted Residue
Kodar-Polyester	A polymer of para disubstituted aryl esters tentatively identified as a co-polymer of terephthalic acid and

Film	Infrared Identification of Extracted Residue
Kodar-Polyester (cont'd)	ethylene glycol. It was not possible to determine if these residues contain low molecular weight film fractions.
Lexan-Polycarbonate	A mixed polyester resin of phthalic and terephthalic acids and ethylene glycol. The residues may contain a small amount of low molecular weight polycarbonate polymer. Phenol and/or bisphenol-A is evident in some spectra.
Rilsan-Polyamide (Nylon 11)	A mixed polymeric resin suspected as a phthalic and terephthalic acid-ethylene glycol co-polymer.
Teflon-Fluorocarbon	A polyester resin suspected as a terephthalic acid-ethylene glycol co-polymer.

5. Microscopic Examination of Extracted Films

Results of all microscopic examinations are summarized in table form below. Two general statements are applicable to the results shown.

(a) The dissolution of laminated foil with HCl or NaOH on three of the four films in general left the laminating adhesives in place on the film and presumably unchanged. Kodar delaminations left little observable adhesives.

(b) No changes to the films were observed by HCl delamination except for the Rilsan-polyamide film. It apparently reacts with HCl and becomes opaque and white. NaOH delamination of Rilsan had no apparent effect on the film.

Reference samples for all comparative examinations were unlaminated samples of each film material that were not heat processed in any way.

Lexan-Polycarbonate

Sample	Miscroscopic Observations
Unlaminated Reference, no treatment	Clear film showing no structural pattern in plane polarized light, birefringent in crossed nicols.

Lexan-Polycarbonate
(cont'd)

Sample	Microscopic Observations
Unlaminated Reference, HCl treated	No observable change from untreated reference
Laminated Control HCl delaminated, not extracted	The film has a structural pattern described as rough or puckered and labeled as a lamination adhesive structure; probably formed in heat lamination process. Laminating adhesive distributed on entire surface without voids or open spaces but with the roughness cited above. Film is birefringent in crossed nicols.
HCl Delaminated, 150°F., 2 hr heptane extracted	No apparent change from laminated control.
HCl Delaminated, 150°F., 16 hour heptane extracted	No apparent change from laminated control.
HCl Delaminated, 250°F., 2 hour heptane extracted	Laminating adhesive structure present but scattered cavities or depressions in the film are evident where the laminating adhesive is not uniformly distributed. Birefringence effect in crossed nicols is weak.
HCl Delaminated, 250°F., 8 hour heptane, extraction attempt (not extracted - all pouches ruptured)	No apparent change from laminated control (not extracted therefore no extraction effects)
HCl Delaminated, 250°F., 2 hour water extracted	No apparent change from laminated control.
Kodar-Polyester	
Unlaminated Reference, no treatment	Clear film showing no structural pattern in plane polarized light, birefringent in crossed nicols.
Unlaminated Reference, HCl treated	No structural changes evident, crossed nicol birefringent color intensity somewhat less than untreated control.

Kodar-Polyester
(cont'd)

Sample	Microscopic Observations
Laminated Control, HCl delaminated, not extracted	No evidence of adhesive remaining and no evidence of an adhesive-related film surface change in structure. Appears essentially unchanged from the reference samples, HCl treated.
HCl Delaminated, 150°F., 2 hour heptane extracted	No apparent change from laminated control.
HCl Delaminated, 150°F., 16 hour heptane extracted	No apparent change from laminated control.
HCl Delaminated, 250°F., 2 hour heptane extracted	Some adhesive evident in spots or grouped areas. Definite appearance of cavities or pits throughout film. Birefringence changes in crossed nicols are very non-distinct indicating possible crystal realignment.
HCl Delaminated, 250°F., 8 hour heptane extracted	Appears exactly as 250°F. 2 hour extract sample.
HCl Delaminated, 250°F., 2 hour water extracted	Appearance of many small cavities or pits in groups or bundles, no evidence of adhesives. Crossed nicol points of extinction are normal.
Rilsan-Nylon 11	
Unlaminated Reference, no treatment	Clear film showing no structural pattern in plane polarized light; birefringent in crossed nicols.
Unlaminated Reference, HCl treated	Film becomes opaque with HCl treatment.
Unlaminated Reference, NaOH treated	No apparent change from untreated reference sample.
Laminated Control, NaOH delaminated, not extracted	Very thick adhesive present, giving a rough, matted structural pattern on the surface of the film. The film is birefringent in crossed nicols.
NaOH Delaminated, heptane extracted at 150°F., 2 hours, 150°F., 16 hours, 250°F., 2 hours, 250°F., 8 hours	All samples not distinguishably different from the laminated control, any changes possible are masked from observation by the thick adhesive.

Rilsan-Nylon 11
(cont'd)

Sample	Microscopic Observations
NaOH Delaminated, 250°F., 2 hour water extracted	General microscopic appearance same as the laminated control. This film is partly opaque and white, indicating some change takes place with exposure to water at high temperature.
Teflon-Fluorocarbon	
Unlaminated Reference, no treatment	Clear film showing no structural pattern in plane polarized light, birefringent in crossed nicols.
Unlaminated Reference, HCl treated	No observable changes from untreated reference.
Laminated Control, HCl delaminated, not extracted	Smooth and transparent adhesive distributed in patches and shows no definite structural pattern. No observable changes in film compared with treated reference sample.
HCl Delaminated, 150°F., 2 hour heptane extracted	No observable change from the laminated control.
HCl Delaminated, 250°F., 2 hour heptane extracted	No observable change from the laminated control.
HCl Delaminated, 250°F. 2 hour water extracted	Film is partially opaque. Birefringence changes in crossed nicols indicate partial realignment of crystals. Many small cavities or pits evident throughout film.

These microscopic observations on extracted films indicate a possible explanation for the different amounts of extractives obtained from each film. Where large amounts of extracted residues were obtained from a given film relative to the other three, for example, a corresponding change in microscopic film appearance is also evident. Conversely, where cavities or pits in the film surface appeared after extraction, the extraction yields were relatively higher. Films that turned partially opaque during water extractions (Rilsan and Teflon) show higher water extractions than films that did not become opaque.

Since the major extractives from all films of this study were laminating adhesives (See infrared identifications of extractives.), these materials must in some way pass through the films to be extracted. Structural changes in the films due to high temperature exposure is obviously one possible explanation for allowing migration.

6. Volatile Extractives

Initial, direct gas chromatographic examination of unevaporated 150°F. heptane extracts of all film materials showed none to contain detectable volatile components. Detectable limits of volatiles were established as 0.5 ppm in heptane or better based on prepared reference standards of n-pentane in n-heptane. There were absolutely no quantitative or qualitative differences evident between these film extracts and solvent blanks.

Since heptane extracts of these films made at 250°F. gave the highest total non-volatile extractive levels of any procedure used in this study, these extract conditions were selected for additional studies on the existence of volatile components. The following results were obtained on direct, GC examination of these accelerated extracts:

(a) The Lexan and Rilsan heptane extracts contained no detectable volatile components not common to the solvent blanks.

(b) The Teflon, 250°F., 2 hour heptane extracts contained minor contamination. Four components which elute from the GC column before n-heptane are evident. Based on the n-pentane calibration curve described, the total contamination is estimated at 1 ppm. The largest contaminant (about 75% of the total contaminant peak area) has the same retention time as n-pentane.

(c) The Kodar 250°F., 2 hour extract contained the same four contaminants as Teflon, which were not evident in the solvent blank. With Kodar, the three minor peaks again are estimated at 0.25 ppm. The larger contaminant, having the retention time of n-pentane, is about 4 ppm in the Kodar extract.

It appears from the above studies that none of the films included in this project produce volatile extractives in excess of 0.5 ppm of the extracting

solvent using standard extraction temperatures. Since federal regulations on extractives imply that heptane is an accelerated simulated food solvent in itself, the volatile extractives found in the grossly accelerated heptane extractions (250°F.) are considered very small. Since extraction conditions required to even produce detectable volatiles are greatly in excess of standard test conditions, no attempts were made to identify the volatiles observed in the two film extracts where seen.

D. Summary of Solvent Extractions

1. Extraction yields vary among the four films tested with both water and n-heptane solvents. Some films give higher yields with water relative to the other films, others with heptane.

2. Extraction yields from all films are higher at higher extraction temperatures.

3. Extraction yields are not a function of extraction time beyond two hours at low extraction temperature, but yields may be related to time during high temperature solvent extractions.

4. Extraction yields of the four films tested are all considerably less than maximums specified in Federal Regulations even at extraction conditions in excess of regulation procedures. Therefore, no attempt was made to determine the pharmacological significance of any residues found.

5. All extractives from foil laminated Kodar, Rilsan and Teflon films by both solvents are from the foil laminating adhesives.

6. Extractives from foil laminated Lexan film are predominantly from the laminating adhesives but also show traces of low molecular weight film fractions.

7. All films yielding measurable residues by a particular extraction procedure show microscopic changes in film structural patterns that may be correlated with extraction yields.

8. At solvent extraction temperatures specified in present regulations, no volatile extractives were evident from any of the four films tested (detectable limit - 0.5 ppm). At greatly accelerated extraction temperatures (250°F.), Teflon and Kodar film extracts showed traces (up to 4 ppm) of volatile contamination.

III EXTRACTABLES BY FATS OR OILS:

A. Introduction

In addition to solvent extractions of film materials described previously, this project is concerned with the detection and measurement of film extractables by fats that have been in contact with packaging films during high temperature, food processing conditions. The ultimate objective of this project phase is to determine the validity of an apparent assumption in existing regulations regarding film extractives. This assumption is that film extractions with n-heptane at 150°F. for 2 hours result in amounts of residue five times larger than those obtained by extraction with oil for 2 hours at 250°F. This fixed ratio assumption apparently has not been fully investigated or validated and, in part, is a subject of this study.

The principal limiting factor in assessing the validity of the fixed ratio assumption is the lack of developed procedures for determining film extractives in fat or oil. The development of suitable procedures for these determinations therefore required the major experimental efforts. The general approach used in this endeavor was to evaluate various analytical procedures for applicability to the problem and pursue those applicable to ultimate methods.

B. Evaluations of Analytical Procedures for Problem Applicability

Evaluations of different procedures were made either on fat extracts of the various films (the same four films included in the solvent extraction studies) or on simulated extracts prepared by adding heptane extracted film residues to the fat. It is assumed throughout this study that film residues extracted by fat are the same as those extracted by n-heptane. Fat extractions were made at 250°F. or higher in the manner described for solvent extractions. Both cottonseed oil and a hydrogenated lard were used in these trials. Where required, details on specific samples and sample procedures are given in the description of each method tried.

1. Direct Spectrophotometric Analysis

(a) UV Scans

Prior scanning of heptane extracts of all films indicated absorption of residues in the UV although no specific absorption assignments were made. It was

hoped that the oil extractions of these films would absorb strongly enough to be detected where absorption due to oil was minimal.

Cottonseed oil extracts of Kodar and Lexan pouches were made at 250°F. for 2 hours. A reference oil sample was similarly heat processed in a glass bottle at the same time to serve as a blank. These oil extracts were scanned in the UV region using a Beckman DK-2 Spectrophotometer with the reference oil as a blank. Similarly, heptane dilutions of the oil extracts versus equally diluted blanks were scanned. None of these analyses were successful because the absorption of oil is very high in the wavelength regions of film residue absorption.

(b) Infrared Scanning

Similar direct scanning of these oil extracts was made in the infrared region. As expected, the spectra obtained showed only fat with no evidence of film residues. Residue concentrations were expected to be too low for detection. There was some evidence of a change in the fat due to high temperature extraction but the changes were also evident in the glass bottle, processed blank.

2. Steam Distillation

Based on the assumption that film extractives may be separated from oil by steam distillation, several attempts were made to isolate extractives by variations in this general technique. Both atmospheric and vacuum steam distillations were tried.

Initial oil extractions of Lexan and Rilsan films (250°F. 2 hour extractions) were strongly suspected of containing film residues. Evidence for this was observed in storage of the oil extractions. The oil from several pouches of each film was collected together in a single glass bottle following extraction and stored at 0°C. in a cooler along with a heat processed blank oil (processed in glass). The two extract samples remained completely liquid for several days at 0° storage while the blank oil began crystallizing after 2-3 hours in the cooler. These samples showing this difference in storage behavior that was presumed due to extractives were used in initial steam distillation residue recovery trials.

(a) Atmospheric Pressure Steam Distillations

An all glass apparatus was used on the two oil extracts just described. This apparatus was a 2-necked sample flask fitted with a steam inlet in one neck and a Dean-Starke trap with a water cooled condenser in the other neck. The open condenser end was fitted to a dry-ice trap to ensure complete condensation. The sample flask was heated with an electric mantle. Steam was generated in a second flask connected to the sample flask with glass tubing. In operation, steam was admitted through the fat extract sample continuously at a rate of 8-10 ml/minute.

Three hundred grams of each oil extract and the heat processed blank were separately steam distilled using 400 ml of water introduced as steam while holding the fat temperature at 250°F. The total condensate of each was extracted 5 times with 50 ml of n-heptane. The combined heptane extracts and the extracted distillates were then evaporated to dryness and weighed. Infrared spectra were made on the residues with the following results:

Extracted Distillate Water

Sample	Weight (g)	Infrared Identification
Oil blank	0.00092	Inorganic salts (water residue)
Lexan Extract	0.00099	Inorganic salts (water residue)
Rilsan Extract	0.00108	Inorganic salts (water residue)

Heptane Extracts of Distillate

Oil blank	0.00046	Glyceride Esters (fat carried over with distillate?)
Lexan Extract	0.00006	No spectra attempted
Rilsan Extract	0.00228	Glyceride Esters (fat carried over with distillate?)

Tri on these extracts were negative regarding film extractive recovery and no further atmospheric steam distillations were made.

(b) Vacuum Steam Distillations

Using an apparatus designed in this laboratory to deodorize shortenings after refining, a vacuum steam distillation was made on a simulated fat extract of Kodar film. This apparatus is an all glass system composed of a mantle heated flask fitted

with a fritted glass steam inlet extending to the flask bottom and a side arm connected to a series of dry ice traps. Vacuum was applied to the whole system at the dry ice traps. Steam was introduced in small increments through a stopcock.

One hundred grams of simulated Kodar extract (containing 2.0 mg heptane extract of Kodar film per 100 g of heat processed blank oil) was distilled in this apparatus at 5 mm Hg vacuum and with the oil at 140°C. (284°F.). Three hundred milliliters of water were admitted to the sample as steam and collected as condensate. As before, the condensate was extracted five times with 50 ml of heptane and the combined extracts were evaporated along with the extracted distillate. The results obtained are as follows:

Sample	Residue Weight	Infrared Identification
Heptane Washed Distillate	0.00081	Inorganic salts (water residue) polyol (probably glycerine)
Heptane Wash	0.00207	Fat, no evidence of extractives

It was concluded from these trials that film residues in the oil extracts evaluated are not recoverable by either atmospheric or vacuum steam distillation. Oil extracts of all films were not evaluated by these procedures but negative results are expected from all based on similarities in film residues by solvent extractions.

3. Solvent Extractions

The concept of separating film extractives from extraction fat by solvent partitioning or solvent extraction was explored using two different solvent systems. Extensive experimental trials were made with one system while basic evaluation trials were made with the second. Each is described separately below.

(a) Dimethylsulfoxide Extractions

The solvent Dimethylsulfoxide (DMSO) readily dissolves unsaturated organic compounds such as the aryl poly-esters of the film extracts. Moreover, it has a low solubility for saturated hydrocarbons and some heterogeneous compounds such as fats or oils. Based on this selective solubility property, DMSO extractions of fat extracts of films were tried as a means to isolate the film residues from the fat.

The procedure used in these trials is briefly as follows: The fat (plus film extractive) sample is dissolved in 50 ml of n-heptane. This solution was then extracted three times with 100 ml of heptane saturated DMSO in a separatory funnel to selectively extract the film residues. The combined DMSO extracts were then washed three times with 50 ml of heptane to remove any dissolved fat. (Film extractives remain with DMSO because of preferential solubility.) The washed DMSO extractives solution is then diluted with 1000 ml of water to reduce the film residue solubility. This aqueous solution was then quantitatively extracted with n-heptane and the heptane extract washed with water to remove entrapped DMSO. The heptane extract was then evaporated to a constant weight.

Using this procedure, trials were made on 25 and 100 gram samples of a cottonseed oil extract of Rilsan film (250°F., 2 hour extraction) and a 25 gram sample of heat processed cottonseed oil only (no extractives). All solvent volumes in these trials were identical. The final yields obtained were different between the trials as shown below. Considerable differences were also seen in the amounts of fat extracted by heptane from the DMSO sample extractions. Apparently, fat solubilities in DMSO were considerably different between the trials.

Sample	Final Yields
100 g Rilsan Extract	18.9 mg
25 g Rilsan Extract	36.7 mg
25 g Oil Blank	457.0 mg

Infrared spectral analyses of these residues indicated only fat in all samples with no evidence of film extractives. UV spectra on the same samples indicate the possible presence of film residues in the extract samples. UV absorptions were weak and masked by fat absorptions. UV quantifications were not possible because of the unknown amounts of fat present.

Because of the unsaturated nature of cottonseed oil fatty acids, the solubility of cottonseed oil in DMSO was reasoned to be higher than a less unsaturated fat. Therefore, repeat DMSO extractions were made using a less unsaturated hydrogenated

lard sample. A 25 gram lard blank (no extractives) and a simulated lard extract of Rilsan film containing 5.0 mg of heptane extracted Rilsan residue/25 grams lard were extracted with DMSO as described above. Yields from these trials were again extremely variable. Evaporated heptane washings of the DMSO-Extractive solutions also showed considerable differences indicating variable DMSO fat solubilities in the trials.

Sample	Final Method Yields (mg)	Total Weight of Heptane Washes (mg)
25 g Lard Only (blank)	3.9	176.3
25 g Lard with Rilsan Extractives	210.6	510.6

The residues from these extraction trials had very complex compositions. By infrared examination, another soluble portion of each (approximately 3/4 of the total residue) was identified as principally saturated triglycerides but with branched chained fatty acid moieties not evident in the parent lard. The infrared spectra of the ethyl ether insoluble portion of each indicated a complex compound containing hydrogen bonded sulfoxide functional groups. This indicates a possible reaction between DMSO and the fat during extraction since the sulfoxide groups observed were chemically bonded in a manner different from DMSO.

Because of the extreme variation in yields by this method and the diverse chemical nature of the residues obtained, no further efforts in this DMSO extraction approach were made.

(b) Acetone Partitioning

Basic experiments were performed to evaluate the feasibility of partitioning film extractives between fat and aqueous acetone. The basis of this approach is as follows:

> Fat (with extractives) is completely soluble in acetone. If water is then added to the solution with continual agitation, the oil becomes insoluble in the resulting acetone-water solution and separates out as a second phase. If the partition coefficient of the film residues between acetone-water and fat were

favorable, the residues would remain with the acetone-water solution as the fat separates. The acetone-water could then be evaporated leaving the film residues.

Assessments of the relative partitioning of fat and extractive residues were made by treating separate acetone solutions of each with water. It was shown in these trials that the same amounts of water were required to separate the extractives of Kodar, Rilsan and Lexan films from acetone-water solution as were needed to separate cottonseed oil. The amount of water needed was independent of the beginning solute (fat and/or film residue) concentration in acetone. It was concluded therefore that no partitioning of film extractives would occur between oil and water-acetone solution. As the oil phase separates from the aqueous solution, the film residues would also separate and remain with the oil. The approach is not applicable therefore as a separating or concentrating procedure.

4. Nephelometric Analyses

Karel and Wogen (2) reported some success in measuring polyester film extractives by oils using nephelometric or turbidometric analyses. The basis of this procedure is a precipitation of a portion of the extractives from the oil on adding an ethyl-isopropyl alcohol mixture to the oil followed by a measure of turbidity in the sample.

Trials by this technique were made on oil extracts of Kodar, Rilsan and Lexan films (250°F., 2 hour extractions). Samples of these extracts were diluted with an equal volume of heptane and mixed with ethyl and isopropyl alcohols. The samples were examined in a Pfaltz and Bauer Turbidometer.

None of the oil extract samples gave turbidometer readings that were different from the oil blanks. Apparently, the concentrations of film extractives in the samples were too low to give measurable turbidity. As a result of these negative findings, this approach was abandoned.

5. Freeze Concentrations

As a means to isolate or at least concentrate the film residues from fat, a technique used by McKinley et al for isolating pesticide residues from fat was tried

(4)(5)(6)(7). In this freeze concentration technique, fat extracts are dissolved in solvent and the solution cooled to crystallize the fat. Film residues remain in solvent solution and they are separated from the fat crystals by filtration. Residues are subsequently recovered from the filtrate by solvent evaporation.

Initial application of this technique showed immediate merit and extensive investigations on the procedure were made. Complete isolation of film residues from fat were never achieved but the method proved very useful as a residue concentration procedure. Concentrates of residues so obtained were further investigated by a number of procedures which are described later.

All fat crystallizations were done in acetone solutions at -70°C. This cooling was done in Erlenmeyer flasks immersed in a dry ice-methyl cellosolve bath. Following crystallization, the fats were filtered with vacuum in a jacketed Buchner funnel cooled to -70°C. by dry ice cooled methyl cellosolve circulating in the jacket. Circulating pumps and other equipment were similar to those described in the references cited.

Crystallized fats were redissolved and recrystallized to ensure complete residue removal. Filtrates were similarly recooled in efforts to recrystallize and remove any dissolved fat. Sample sizes, solvent volumes, crystallizing times and temperatures and filtering procedures were all investigated to optimize separation of residues. The detailed procedure resulting from these efforts is summarized below. Essentially, three separate crystallizations were used for each sample which are labeled (a) (b) and (c).

(a) Twenty-five grams of fat extract were dissolved in 400 ml of distilled acetone. This was cooled with slow agitation to -70°C. and held at this temperature for 20 minutes. The slurry obtained was filtered with vacuum through Whatman #42 filter paper in a -70°C. Buchner funnel. The fat crystals were tamped with a -70°C. beaker bottom to aid removal of entrapped solvent and then washed with 25 ml of -70°C. acetone. The washes were collected with the filtrate. This filtrate was labeled number 1.

(b) The crystallized fat from (a) above was carefully transferred from the Buchner funnel to a clean Erlenmeyer flask and redissolved in 300 ml of distilled

acetone. The solution was again crystallized at -70°C. for 20 minutes, filtered, tamped and washed with 25 ml of -70°C. acetone. This filtrate was labeled number 2. The filter cake was discarded.

(c) Filtrate number 1 was recooled to -70°C. for 20 minutes and filtered in the same manner as (a) and (b) using a clean Buchner funnel. The filtrate was collected in the same flask as filtrate number 2 and evaporated together on a steam bath. Final evaporations were made in 15 ml glass beakers in a 100°C. oven for 30 minutes before desiccator cooling and weighing.

Initial trials at freeze concentration were made on samples of cottonseed oil only (with no extractives) and heptane extractives of two films only (no fat). These trials were made to test the procedure for fat removal and residue recovery, respectively. The results shown below were encouraging for both sample types. The film residue sample sizes may be much larger than anticipated from a 25 gram fat extract sample, but recovery data should be independent of sample size.

Sample	Freeze Concentrated Residue Weight (grams)	% Recovery
25 g Parent Cottonseed Oil	0.34536	1.38
0.01306 g Heptane Extract of Lexan	0.01302	99.79
0.00432 g Heptane Extract of Kodar	0.00394	91.20

The freeze concentrated residue from a cottonseed oil extract of Lexan pouches (250°F., 2 hour extraction) was obtained next by this procedure, and it yielded 0.25740 grams of residue. Infrared examinations of this residue and the parent oil residue above revealed the principal composition of both was mixed mono- and diglycerides which are selectively separated from the original glyceride oils in freeze concentrations. This identification is confirmed in the literature (9). Probably because of their low concentration, no evidence of film residues were seen in the extract sample spectrum.

Attempts were made next therefore, to reduce the fat concentration in the freeze concentrated residues by improving the fat filtering efficiency. Filter beds of both carbon and cellulose were tried as fat retardants along with diatomaceous earth

filter aids. Samples of cottonseed oil and film residues were used separately in these trials. Results obtained showed no effect in better oil removal with filter aids and cellulose beds and, while carbon reduced the oil residue, it also absorbed most of the film residues.

Freeze concentration trials using longer freezing times and different freezing temperatures were made next in efforts to reduce post-freeze fat residue. Temperature variation efforts were specifically directed toward fractionating the oil into freezable and non-freezable portions; the former to be subsequently used as a film extracting oil.

Results obtained from three trials with cottonseed oil using 40, 60 and 120 minutes freeze times at -70°C. showed no significant improvement in fat residue reduction over 20 minute freezings. The results of freezing temperature variations were similarly negative. At freeze temperatures of -60, -50 and -40°. (for 20 minutes) crystallized fat yields were proportionately smaller at the warmer temperatures than at -70°C. Redissolving and refreezing these crystallazed fats, however, revealed that post freeze residues from each were about equal to those from the parent fat. It was concluded therefore that neither of these approaches was useful in improving freezing efficiencies. Methods were therefore investigated to further clean up the freeze concentrated residues obtained by the standard procedure given previously.

Column chromatographic methods were extensively tried as a clean-up procedure. Both absorption and partition systems were used with a variety of solvents and solvent combinations. A summary of the systems tried is tabulated below. Samples used in the various trials included freeze concentrated simulated fat extractions (heptane extractives added to freeze concentrated fat only), freeze concentrated fat only and film residues only. All column eluate fractions were 100ml except where indicated.

SUMMARY OF COLUMN CHROMATOGRAPHY SYSTEMS USED

Column	Solvent System	Solvent Ratios/Fraction (V/V)
Silica gel	Benzene-Ethyl Ether	100B, 90B/10EE, 80B/20EE, 100EE
Silica gel	Benzene-Acetone	100B, 80B/20A, 50B/50A, 100A
Silicic acid	Benzene-Acetone	100B, 80B/20A, 50B/50A, 100A
Silicic acid	CH_2Cl_2-Petroleum Ether-Acetone	15C/85P, 30C/70P, 50C/50P, 50A/50P, 100A
Silicic acid	CH_2Cl_2, Petroleum Ether-Ethyl Ether	60C/40P, 70C/30P, 90C/10P, 100C, 90C/10EE, 80C/20EE, 70C/30EE, 60C/40EE, 50E/50EE, 100EE
Silicic acid-Celite(1)	CH_2Cl_2-Ethyl Ether	98C/2EE, 96C/4EE, 94C/6EE, 92C/8EE, 90C/10EE, 80C/20EE, 100EE
50 g Fluorosil(2)	Hexane-Chloroform-Acetone	100H, 99H/1C, 98H/2C, 95H/5C, 90H/10C, 80H/20C, 74.5H/25C/0.5A, 74H/25C/1A, 73H/25C/2A, 71H/25C/4A, 67H/25C, 8A, 60H/25C/15A, 20H/50C/30A, 50C/50A

(1) Several trials by this system were made using elution volumes of 100, 80 and 75 ml fraction.

(2) Elution volumes were 75 ml/fraction. This chromatographing system was patterned after Patchett and Batchelder. (8)

Results obtained from these many column chromatographic clean-up attempts were generally unsatisfactory. As previously mentioned, the freeze concentrated residues of cottonseed oil are predominantly monoglycerides with some diglycerides present. These fats apparently have a polarity very similar to the film residues and complete column chromatographic separation of the two were never realized in any of the trials made. Without exception, regardless of the column system, any elution of film residues were accompanied by a fat elution and both were eluted together as multiple fractions.

Cottonseed oil was replaced in freeze-concentration trials with a hydrogenated lard. Twenty-five grams of this fat gave an 0.037 g residue in freeze concentration versus an average yield of 0.355 g from 25 grams of cottonseed oil. This favorable, 10 fold reduction in residue yield suggested two additional procedures for the analysis of freeze concentrated residues.

1. Thin Layer Chromatography

Thin layer chromatography trials were made on freeze concentrated samples of heat processed lard only (processed in a glass bottle) and the heptane extracted residues of all four films. Silica Gel G plates, 250 microns thick, were used with a plate developing solvent of 70 volumes of ethyl ether, 35 volumes of petroleum ether and 0.5 volumes of acetic acid. Other solvent systems were also tried but with lesser success. Thin layer chromatography spot development was by iodine vapors and/or a spray of 20% recorcinol followed by 4N H_2SO_4.

The residues of all four films showed nearly identical separation by thin layer chromatography. Up to nine components were revealed in each film's residue depending upon the amount of sample applied to the plate. Speculatively, these components are polymeric resins of different chain length. The separated fractions were of varied concentrations or spot densities between the different film residues but in all sample separations, one component, common to all film residues, greatly predominates in concentration. With a minimum residue sample application to the plate for visual spot observations (20 micrograms), only this one major component is evident in the extractive residue of all films.

Thin layer chromatography separations of heat processed, freeze concentrated, lard only residues similarly show several components. In general, the retention times of the fat components were less than film residue components and they advance faster on the plate during solvent development. When fat and film residues are spotted separately on the same plate and developed in parallel, the major residue component mentioned above appears at a different point of advancement than any fat components. Simulated fat extracts (heptane film extractives added to fat), however, showed a different pattern. When fat and residue are combined in the same plate spot and developed together, only partial separation of each is achieved and the major residue component partly overlaps a major fat component. There is an apparent attraction between these fat and residue components which alters the retention times of both. This same phenomena occurs with actual fat extract samples.

Since the film residues separate into a number of components not entirely resolved from fat components by thin layer chromatography, this method could be adapted to only semi-quantitative use at best. The thin layer chromatography approach has an obvious qualitative use however in examining fat extracts of pouches for residues. To test this application, a lard extract of Rilsan film (275°F., 2 hour extraction) was separated on a preparatory TLC plate. The freeze concentrated residue was streaked across a plate and developed in the normal manner. The area of the major film component, identified from a parallel developed single Rilsan residue spot, was scraped from the plate and the scrapings extracted with acetone. The acetone was evaporated off from this extract, and it was redissolved volumetrically in n-heptane for UV examination. The UV spectra showed the same qualitative absorptions as the heptane extracted residue of Lexan but it also showed the presence of fat. Since the fat composition and concentration was unknown, quantitative compensation was not attempted.

It was apparent from the above trials that thin layer chromatographic analyses of freeze concentrated residues could be used as a qualitative test for film residues. The method has limiting disadvantages in a quantitative application however and therefore other systems were investigated.

2. Quantitative Infrared Methods

Direct infrared examinations of freeze concentrated residues of lard extracts in CS_2 solution showed evidence of film residues in addition to lard residues. There was sufficient evidence to believe that the residues could be quantitatively evaluated with calibration data and this approach was subsequently investigated. The efforts are described in paragraph C below which includes quantitative results obtained on the four films of this study.

C. Quantitative Measurements of Film Residues in Fat

In the method evaluations described in the previous section, the combination of freeze concentration and quantitative infrared methods appeared as the most promising techniques found for determining film residues in fat extracts. This approach was pursued therefore in evaluating fat extracts of the four films in this study. In the

freeze concentration experiments described, it was evident that a hard fat was preferred for pouch extractions to minimize post-freeze fat residues. In the efforts described below therefore, the hydrogenated lard reported previously was used throughout and the freeze concentration technique described in the previous section was used without change.

All quantitative infrared evaluations were made on a Beckman IR-4 Spectrophotometer. From comparisons of spectra on freeze concentrated fats and the individual film residues obtained by n-heptane extractions, the absorption band at 12.05 microns was selected for quantitative analyses. For the film residues, this band is the out of plane -CH deformation vibration of a para disubstituted benzene ring. At this wavelength, freeze concentrated fats also show a small absorption and consequently the absorptivities of each component were determined. All spectra were obtained in carbon disulfide solution in a 1.005 mm cell with CS_2 in the reference beam. Band absorptions in all samples were calculated from the minimum band transmission at 12.05 microns to the maximum transmission between 12.5 and 13.0 microns. This technique was used to minimize errors caused by the CS_2 band at 11.7 microns. Spectrophotometer constants for all infrared analyses were as follows:

Single beam to double beam ratio:	2:1
Period:	2 seconds
Scanning Speed:	0.5 microns/minute
Slit Width:	0.8 mm
Band Width at 12 micron band:	0.5 microns

Calibration samples for infrared analyses were prepared by adding serial dilutions of heptane extracts of films to freeze concentrated residues of a heat processed lard blank. This fat was heat processed in a glass bottle at the same time as fat extracts of pouches which are described later. Acetone was used to add the film residues to the freeze concentrated blank fat residues and then evaporated off. Because of sample and time limitations, calibration samples were prepared with only Lexan and Rilsan film residues. Also, only two concentration levels for each film residue were prepared. These were considered sufficient because of the similarity

of the film residues involved. Calibration sample compositions are shown below.

Sample	Weight of Freeze Concentrated Blank Fat (mg)	Weight Film Residue Added(mg)	Calculated Residue %
Rilsan-1	29.40	1.21	3.96
Rilsan-2	22.14	1.34	5.70
Lexan-1	23.10	0.35	1.49
Lexan-2	27.48	0.82	2.90

These calibration samples, along with samples of Rilsan and Lexan film residues only and freeze concentrated residues of blank fat only were quantitatively dissolved in CS_2 and their spectra obtained. From these spectra, absorptivities of fat and film residues were calculated with the following results.

Sample	Absorptivity (liters/g cm)
Lexan Film Residue	0.90
Rilsan Film Residue	0.85
Blank Fat (containing no extractives) and Fat in Lexan Calibration Samples	0.020
Fat in Rilsan Calibration Samples	0.005

It is seen that the film residues have nearly the same absorptivities but that there are differences in the calculated fat absorptivities depending on the source of the fat. The fat in the Rilsan calibration samples apparently changed on addition of the film residues to materially decrease its absorptivity. The observed values are not attributed to analytical error for additional data presented in recovery studies described later substantiate their validity.

To evaluate the recovery of film residues in the freeze concentration procedure, heptane extracted film residues were added in known concentrations to 25 gram samples of heat processed lard only and freeze concentrated together. Four samples were prepared having the following compositions.

Residue Added	Wt of Fat (g)	Wt of Residue Added (mg)	Total Freeze Concentration Residue (mg)	Residue % Assuming 100% Recovery
Rilsan A	25	1.2	27.76	4.3
Rilsan B	25	1.8	26.98	6.7
Lexan A	25	0.8	24.37	3.3
Lexan B	25	1.2	24.17	5.0

The freeze concentrated residues shown were quantitatively dissolved in CS_2, and their spectra obtained. Film residue concentrations were calculated from their respective spectra using the fat and film absorptivities determined previously in the calibration samples. Results are shown below.

Recovery Sample	Residue Concentration in CS_2 Solution Assuming 100% Recovery (mg/ml)	Fat Absorptivity (liters/g cm)	Measured Film Residue Concentration (mg/ml)	% Yield
Rilsan A	1.25	0.0005	1.25	100
Rilsan B	1.91	0.0005	1.65	86
Lexan A	0.83	0.020	0.82	99
Lexan B	1.16	0.020	1.08	93

The data show that approximately 90 to 100 percent of the film residues in fats are recovered in freeze concentration. Similar results were obtained in earlier freeze concentration recovery trials on residues alone reported in the procedure evaluation section. No differences in recovery of Lexan and Rilsan residues are expected because of their very similar compositions and it is reasonable to conclude that the fat absorptivity of 0.005 liters/gram cm used for Rilsan extracts is correct based on the recovery results obtained. A Rilsan residue recovery of only 64% results if the Lexan fat absorptivity (0.020 1/g cm) is used for the calculation which is not consistent with previous data.

Hydrogenated lard extractions of Kodar, Lexan, Rilsan and Teflon pouches were made at 275°C for 2 hours in the manner described for solvent extractions. This temperature was judged the maximum temperature compatible with the films based on repeated failures in extraction attempts at higher temperatures (300°F.). As in solvent extractions, a constant ratio of 2 ml of extractant (lard) per in^2 of pouch surface was used. The lard had a density of 0.870. The Kodar and Teflon pouches were sealed within Mylar pouches as before. A lard sample was also processed in a glass bottle at the same time to serve as a blank.

Twenty five gram samples of these fat extracts were freeze concentrated and the total freeze concentrated residue weights determined as shown below. The variability

in weights for these and all freeze concentrated residues reported is due primarily to fat yield differences in freeze concentration.

Film Extract	Freeze Concentration Residue Weights (grams)
Kodar	0.03553
Lexan	0.04878
Rilsan	0.03384
Teflon	0.02796

These freeze concentrated residues were quantitatively dissolved in CS_2 and their respective spectra obtained. The spectra of all samples showed an absorption band at 12.5 microns which was not present in any previous spectra including that of the heat processed fat blank. This indicates a probable change in the fat during pouch extraction which is associated with the films and confirms previously described observations on fat modifications during extraction. It is not known if the fat absorptivity of the 12 micron band is also changed.

Film Extract	Absorptivity (l/g cm)
Kodar	0.013
Lexan	0.018
Rilsan	0.022
Teflon	0.013

Using the equation

$$A = a_F c_F + a_R c_R$$

the film residue concentrations in these fat extraction samples were calculated. In the equation, A is the absorption per unit cell length, a_F and a_R are the absorptivities of fat and film residue respectivel and C_F and C_R are their corresponding concentrations. For the absorptivities of Kodar and Teflon film residues, a value of twice the Lexan and Rilsan value was taken assuming the para disubstitution of these film residues is two times that of the Lexan and Rilsan residues. This assumption is based on the infrared identifications of heptane extracted residues discussed previously.

Calculations of all residue concentrations were made using all fat absorptivity values obtained in the calibration data. Therefore, both 0.020 and 0.005 1/g cm values obtained from the Lexan and Rilsan calibration samples respectively were used for all samples. In addition, a fat absorptivity value of 0.013 1/g cm was included. This value is obtained from the Kodar and Teflon extract sample absorptivity if one assumes that these extracts contain no film residues. Results shown therefore include a range of residue levels possible based on all experimental data.

		Measured Milligrams of Film Residue/25 g Fat Extract		
Film	Fat Absorptivity	0.020	0.013	0.005
Kodar		0	0	0.12
Lexan		0	0.23	0.58
Rilsan		0.07	0.25	0.45
Teflon		0	0	0.09

It has been shown earlier that the fats in calibration samples with residues of different films have different absorptivity values. Also, as previously mentioned, the fats of all the film extract samples were seen to be chemically different than both calibration samples and blank fat samples at least in the 12.5 micron region. It is not known what changes, if any, have occurred in the fat absorptions of these extract samples in the 12.05 micron band. If one assumes however, that the minimum fat absorptivity observed at 12.05 microns in the calibration samples similarly occurred in all fat extract samples, then the maximum film residue concentration is obtained. Therefore, the residue concentration results above, obtained with the 0.005 1/g cm absorptivity value for fat, are considered the maximum film residues possible in the samples analyzed.

These results were recalculated in the units of concentration used to express extractives in the previous section on solvent extractions. These units are mg of extractives per square inch of exposed film surface and ppm of extractives in the extractant as shown below.

Film	Maximum Extractables (mg/in^2)	Maximum ppm in Extracting Fat
Kodar	0.0083	4.7
Lexan	0.0403	23.3
Rilsan	0.0312	18.0
Teflon	0.0063	3.6

The ratio of heptane extractables at 150°F to fat extractables at 275°F were calculated from these results. Heptane extractables are shown in Table III.

Film	Ratio of Heptane Extractables at 150°F to Fat Extractables at 275°F.*
Kodar	0.289
Lexan	0.101
Rilsan	0.127
Teflon	0.468

D. Summary of Fat Extraction Analyses

Several analytical procedures were evaluated to determine film residues in high temperature fat extracts of the films. A combination of film residue concentration by freezing out the extracting fat and quantitative infrared analyses of the concentrates showed the most promise as a workable method. These techniques were applied to high temperature fat extracts of the four films of this study with the following general results:

1. Freeze concentrations of film residues from fat extracts or simulated fat extracts give approximately 99.88% removal of fat and 90-100% recovery of film residues.

2. Fats remaining with film residues after freeze concentration are varied in composition according to their previous processing and/or associations with film residues.

3. Quantitative infrared analyses were made using the 12.05 micron absorption band of the film residues. Since freeze concentrated fat residues also absorp at this wavelength, analyses were made by determining the absorptivities of both fat and film residues in calibration samples and applying these values to extract samples.

4. Fat absorptivities at 12.05 microns were found to vary between freeze concentrated calibration samples containing different film residues. Similarly, the fat

* Fat extractables are the maximum possible amounts in the sample extracts analyzed.

absorptivities of freeze concentrated film extracts were suspected of differing from both calibration and blank fat residues. Extract sample fats are known to be different from non-extract fats.

5. Because of observed variations in infrared fat absorptivities among the various samples analyzed, film residue concentrations in the extract samples were also uncertain up to a maximum possible concentration level. For comparisons with heptane extraction results therefore, film residue concentrations in unknown fat extract samples were calculated on the conservative, maximum possible film residue basis.

E. Conclusions

From results obtained, it appears that the ratio of heptane extractables at 150°F. to fat extractables at 275°F. varies from film material to film material and is not fixed. Moreover, in the films examined, the ratio is considerably less than the 5:1 value expressed in paragraph 121.2514 specifications. At high temperatures, film residues are extracted in greater amounts by fat than by heptane at 150°F. indicating that film extraction is a function of temperature to a substantial degree and perhaps a lesser function of the extracting solvent.

IV. SUGGESTIONS FOR FUTURE RESEARCH:

In the present project, the so-called film residues extracted, were identified principally as laminating adhesives which migrate through or permeate the films. An exception was the Lexan-polycarborate residues which showed traces of film degradation products. Results obtained in this study therefore, generally represent adhesive migration through the films during extraction and do not reveal significant differences in the stabilities of the films themselves. All films studied appear to have excellent thermal stability with regard to extractable breakdown products.

Assuming foil laminations of these films are required for food packaging uses, further studies in laminating adhesive migrations may be desired. Parameters of study should include adhesive migration dependence on

(a) Film thickness

(b) Film density

(c) Type and amount of adhesive used

Additional studies on the mechanism of migration would be needed also for simple film permeation may not be indicated.

The four film materials investigated in this project indicate excellent potential application as food packaging materials from a film residue migration standpoint. Before their application to routine food processing use however, additional development is required to obtain pouch sealing reliability. Sealing methods or general pouch manufacturing techniques which give stable pouches for high temperature processing are definitely required. In this study, the Kodar and Teflon film pouches were considerably less reliable than the Lexan and Rilsan pouches, but all are amenable to additional studies on sealing requirements.

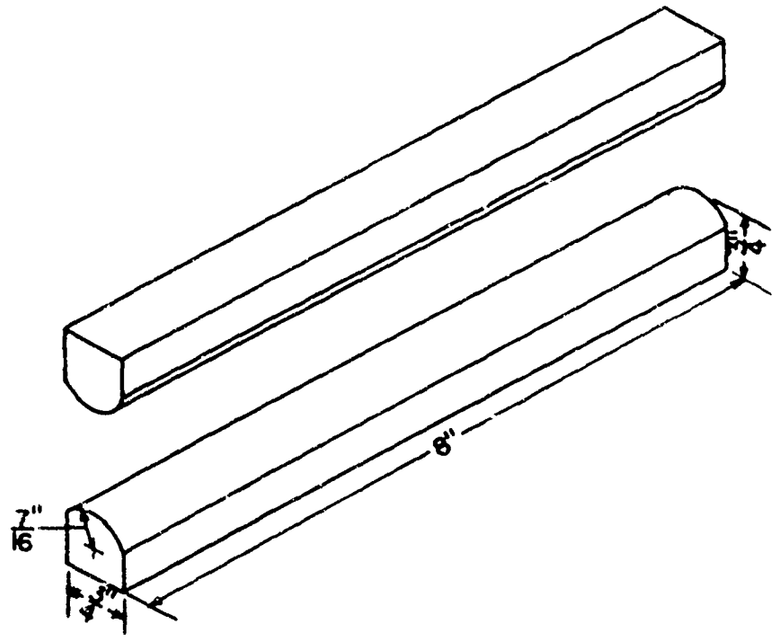

FIGURE 1 ISOMETRIC PROJECTION OF 7/16" RADIUS ROUND BARS FOR ROBOT PARALLEL JAW BAR SEALER

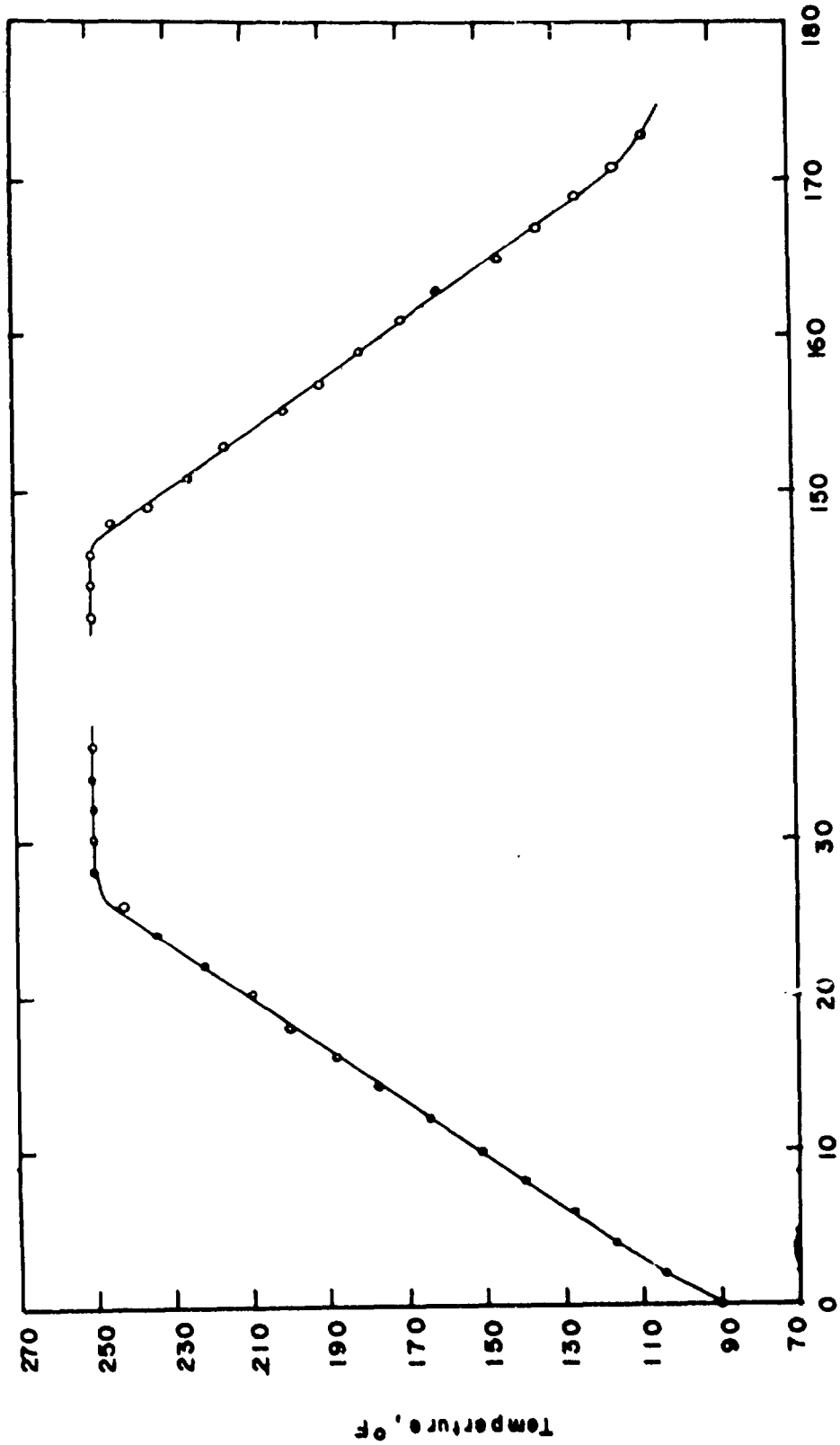

FIGURE 2 HEATING AND COOLING CURVES FOR A 250° F. EXTRACTION: ROOM TEMPERTURE TO 250° F.

TABLE I. RESULTS OF SCREENING TESTS ON LAMINATED FILMS

IMMERSION IN 300°F. VEGETABLE OIL BATH

	Sample	Observations After Heating
1.	Milprint Polypropylene (inside)	Crumbling, dissolution and delamination
	Mylar (outside)	No apparent change
2.	Dow 1302 Polyvinyl (inside)	Discoloration to nearly black
	Unknown (outside)	Delaminated
3.	General Electric Lexan Polycarbonate	No apparent change
4.	Schjeldahl Capron Nylon	No apparent change
5.	May Industries Rilsan-Nylon 11	No apparent change
6.	Dow Mylar (outside)	No apparent change
	Polyethylene (inside)	Melted, delaminated
7.	Dow Polyethylene (inside)	Evolved gas, delaminated
	"Aquatuf" (outside)	Blistered, discolored, delaminated
8.	Kodak Kodar Polyester	No apparent change
9.	Allied Aclar-Fluorocarbon	Cracked, split, discolored tan
10.	Dupont Teflon Fluorocarbon	No apparent change

TABLE II. RESULTS OF SCREENING TESTS ON LAMINATED FOILS

SUSPENSION IN 300°F. DRY OVEN FOR 20 MINUTES

	Sample	Observations After Heating
1.	Milprint Polypropylene (inside)	Became brittle, roughened, delaminated
	Mylar (outside)	No apparent change
2.	Dow 1302 Polyvinyl (inside)	Brown discoloration
	Unknown (outside)	No apparent change
3.	General Electric Lexan Polycarbonate	No apparent change
4.	Schjeldahl Capron Nylon	No apparent change
5.	May Industries Rilsan-Nylon 11	No apparent change
6.	Dow Mylar (outside)	No apparent change
	Polyethylene (inside)	Curled and fused
7.	Dow Polyethylene (inside)	Curled and fused
	"Aquatuf" (outside)	Curled and fused
8.	Kodak Kodar Polyester	No apparent change
9.	Allied Aclar-Fluorocarbon	Became brittle
10.	Dupont Teflon Fluorocarbon	No apparent change

TABLE III. RESULTS OF EXTRACTIONS WITH n-HEPTANE FOR 2 HOURS AT 150°F.(1)

Film	Number of Samples(2)	Extractables (mg/in^2) Average	Range	ppm in solvent at 2 ml/in^2	Corrected Values(3) Extractives (mg/in^2)	ppm
Aclar-Fluorocarbon	8	0.00255	0.00210	1.865	0.00051	0.373
Kodar-Polyester	4	0.00240	0.00060	1.745	0.00048	0.349
Lexan-Polycarbonate	4	0.00405	0.00070	3.035	0.00085	0.607
Rilsan-Nylon 11	4	0.00395	0.00120	2.870	0.00079	0.514
Teflon-Fluorocarbon	4	0.00295	0.00075	2.195	0.00059	0.439

(1) Uncorrected for solvent blank. Solvent blank = 0.6 mg/liter. Average sample contained 350 ml heptane.
(2) A sample represents the combined extractions of four pouches.
(3) Correction applied to heptane extracts as presented in admendment published in the Federal Register, February 10, 1962, 27 F.R., 1252, Paragraph 121.2514, Section E, Subparagraph 5.

TABLE IV. RESULTS OF EXTRACTIONS WITH n-HEPTANE FOR 16 HOURS AT 150°F.(1)

Film	Number of Samples(2)	Extractables (mg/in^2) Average	Range	ppm in solvent at 2 ml/in^2	Corrected Values(3) Extractives (mg/in^2)	ppm
Aclar-Fluorocarbon	4	0.00215	0.00170	1.375	0.00043	0.275
Kodar-Polyester	4	0.00165	0.00052	1.035	0.00033	0.207
Lexan-Polycarbonate	4	0.00465	0.00074	3.525	0.00093	0.705
Rilsan-Nylon 11	4	0.00135	0.00018	0.990	0.00027	0.198
Teflon-Fluorocarbon	Not extracted					

(1) Uncorrected for solvent blank. Solvent blank = 0.6 mg/liter. Average sample contained 350 ml heptane.
(2) A sample represents the combined extractions of four pouches.
(3) Correction applied to heptane extracts as presented in amendment published in the Federal Register, February 10, 1962, 27 F.R., 1252, Paragraph 121.2514, Section E., Subparagraph 5.

TABLE V. COMPARISON OF RESIDUE RECOVERY PROCEDURES USING DIFFERENT METHODS OF SOLVENT EVAPORATION (150°F. EXTRACTIONS, 2 HOURS)

Film	Total Residue (mg/in^2)		
	Procedure Method	All Platinum Evaporation	All Glass Evaporation
Kodar Replicates	0.00056	0.00052	0.00044
	0.00044	0.00057	0.00037
	0.00046		
	0.00044		
Lexan Replicates	0.00086	0.00097	
	0.00076	0.00081	
	0.00086		
	0.00090		

TABLE VI. RESULTS OF EXTRACTIONS WITH WATER AT 250°F. FOR 2 HOURS

Film	Number of Samples(1)	Ave. Solvent Volume per Sample (ml)	Expected Water Blank Residue at 2 mg/liter (mg)	Ave. Total Residue per Sample (mg)	Uncorrected Results: Extractables (mg/in^2) Average	Uncorrected Results: Extractables (mg/in^2) Range	Uncorrected Results: ppm in Solvent	Results Corrected for Water Blank: Extractables (mg/in^2)	Results Corrected for Water Blank: ppm in Solvent
Kodar(2) Polyester	4	350	0.70	0.61	0.00386	0.00076	1.93	Less than blank	
Lexan Polycarbonate	4	302	0.61	0.65	0.00426	0.00081	2.135	0.000263	0.13
Rilsan Nylon 11	4	290	0.58	7.28	0.05020	0.01254	25.1	0.04620	23.1
Teflon(2) Fluorocarbon	4	250	0.50	1.315	0.01056	0.00196	5.283	0.00652	3.26
Aclar Fluorocarbon	12	No trials successful							

(1) A sample represents the combined extractions of four pouches.

(2) Extracted by sealing within a Mylar overwrap pouch.

TABLE VII. RESULTS OF EXTRACTIONS WITH WATER AT 275°F. FOR 2 HOURS

(UNCORRECTED FOR SOLVENT BLANK)

Film	Number of Samples(1)	Extractables (mg/in^2) Average	Range	ppm in Solvent at 2 ml/in^2
Kodar(2) Polyester	4	0.0091	0.0013	4.52
Lexan Polycarbonate	7	0.0094	0.0024	4.73
Rilsan Nylon 11	6	0.0669	0.0115	33.46
Teflon(2) Fluorocarbon	2	0.0104	0.0005	5.18

(1) A sample represents the combined extractions of four pouches.

(2) Extracted by sealing within a Mylar overwrap pouch.

TABLE VIII. RESULTS OF EXTRACTIONS WITH n-HEPTANE AT 250°F FOR 2 HOURS AND 8 HOURS(1)

2 Hour Extractions

Film	Number of Samples(2)	Extractables (mg/in^2) Average	Range	ppm in Solvent at 2 ml/in^2	Corrected Values(3) Extractives (mg/in^2)	ppm
Kodar-Polyester	8	0.03605	0.01250	26.485	0.00721	5.297
Lexan-Polycarbonate	12	0.11255	0.03200	82.545	0.02251	16.509
Rilsan-Nylon 11	6	0.03465	0.01150	25.405	0.00693	5.081
Teflon-Fluorocarbon	12	0.00330	0.00205	2.470	0.00066	0.494

8 Hour Extractions

Kodar-Polyester	4	0.03840	0.0100	28.450	0.00768	5.690
Rilsan-Nylon 11	4	0.04650	0.01000	33.220	0.00930	6.644

(1) Results uncorrected for Solvent blank. Solvent blank = 0.6 mg/liter.
Average Lexan and Rilsan samples contained 350 ml.
Average Kodar and Tefion samples contained 250 ml.

(2) A sample represents the combined extracts of 4 pouches.

(3) Correction applied to heptane extracts as presented in the amendment published in the Federal Register, February 10, 1962, 27 F.R., 1252, Paragraph 121.2514, Section e, Subparagraph 5.

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13 ABSTRACT

Solvent extractions were conducted on 4-foil-laminated materials with films of Lexan-polycarbonate, Rilsan-Nylon 11, Kodar-polyester, and Teflon-fluorocarbon. The film residues extracted were principally laminating adhesives which migrate through or permeate the films. An exception was Lexan-polycarbonate which showed traces of film degradation. All films studied appeared to have excellent thermal stability at temperatures up to 275°F. No significant volatile extractives were evident. Extraction yields of the four films tested were all less than maximums specified in Federal Regulations even at extraction conditions in excess of regulation procedures.

Procedures were developed using free fats as simulated solvents. Results gave 90-100% recovery of film residues. The development of the above procedure enabled the assessment of existing FDA regulations regarding film extractives at high temperatures (250°F and higher). The Federal Regulations imply that film extractions with heptane at 150°F for 2 hours result in amounts of residue five times larger than with a food product. From results obtained, it appears that the ratio of heptane extractables at 150°F to fat extractables at 275°F varies from one film material to another and is not fixed. Moreover, the ratio is considerably less than the 5:1 value expressed in the Federal Regulations. At 275°F, film residues are extracted in greater amounts by fats than by heptane at 150°F, indicating that film extraction is a function of temperature to a substantial degree and perhaps a lesser function of the extracting solvent.

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Adhesives	2		9		9	
Residues	2				9	
Flexible	0		0		0	
Films	1		9		9	
Laminated plastics	1		9		9	
Containers	4		4			
Food	4		4			
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